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# The pyrolysis products of vegetable raw materials as a resource for the formation of carbon nanotubes

**Abstract:** The article presents the analysis of the influence which the duration of the mechanical activation of amorphous carbon (1–46 h) has on the morphology of moldable multilayer carbon nanotubes. It has been demonstrated that the prolonged mechanical activation of carbon composite in a vario-planetary mill promotes the formation of aggregates, which entails the loss of the thermal stability of the formed nanotubes when subsequently the vacuum annealing is performed.
*Key words:* pyrolysis, amorphous carbon, mechanical activation, multilayer carbon nanotubes, composite.

## Introduction

Material generated based on carbon nanotubes have unique properties and were therefore find wide application as components of radio electronics, modifiers of structural materials, additives to lubricants, varnishes and paints, hydrogen accumulators of fuel cells of electric cars, high-efficiency adsorbents, gas diffusion layers of fuel cells, etc. [7, 10, 11]. Use of carbon nanotubes in fine chemical synthesis, biology, and medicine is promising as well as for producing composites with improved mechanical and electrophysical properties, including for imparting antistatic and conducting properties to polymers [1, 4, 12].

The properties of amorphous carbon of plant origin and multilayer carbon nanotubes (MCNT), formed during the mechanical activation of the carbon in the vario-planetary mill for 1–27 hours have been studied previously [5, 6, 9].

However, the problem of maximally possible MCNT yield under fixed conditions of mechanical activation of amorphous carbon remained unclarified. This study was carried out to determine the influence of duration of mechanical activation of amorphous carbon on the nanotube content in the end product.


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## Materials and methods

The carbon nanotubes were produced by employing pyrolytic and mechanochemical technologies. Rusty (brown) peat moss *(Sphagnum fuscum)* and Magellan's peat moss *(Sphagnum magellanicum),* shoots of corn of the variety Katerina SV, thorny (spiny) bamboo *(Bambusa blumeana schultes),* cotton plant of the variety Priozernyi (Lake region)-4, and stems (stalks) of okra *(Abelmoschus exculentus)* of the variety Zelenyi barkhat (Green velvet) were used as the feed material. The plant material was initially dried and sieved to remove excess moisture and foreign matters, and disintegrated to 100–150 μm particles. Modifications of carbon having amorphous structure were obtained at 950 °C. The mineral matters were removed from the carbon by chemical washing with a mixture (1:1) of 25% $HNO_3$ and HCl solutions at 100 °C. The treatment was carried out in an analytical autoclave from Wiegand International GmbH (Germany) for 50 min. Next, the amorphous carbon was removed from the mixture of the acid solutions on a Keramtech (Czech Republic) filter and washed with distilled water in an Elamasonic S 30 (Germany) ultrasonic washer for 30 min up to neutral pH (pH 7,0). Thereafter, it was dewatered in a Sigma Laborzetrifugen (Germany) centrifuge and then dried in a Binder drying oven for 60 min at 125–130 °C.

Further, the amorphous carbon was treated in a Fritsch (Germany) Pulverisette-4 vario-planetary mill. The mechanoreactor of the vario-planetary mill consisted of a leak-proof corrosion-resistant steel container with a VK-6 (WC-6) hard alloy insert: the pulverizing bodies were VK-6 hard alloy balls 16 mm in diameter. The mill operation conditions were: rotation speed of main disk 400 rpm and of planetary pinions 800 rpm, intensity (ratio of weight of original materials to weight of pulverizing balls) 1:50.

The specific surface area of the carbon materials was studied on a Sorbtometr-M-series [ZAO (CJSC) KATAKON, Novosibirsk] specific surface area analyzer and the specific surface area was determined by thermal desorption of nitrogen. The X-ray energodispersion microanalysis was performed on an EVO-50XVP (Carl Zeiss) scanning electron microscope in conjunction with an INCA Energy-350 (England) X-ray energodispersion spectrometer. The structure of the MCNT was studied on a Hitachi S5500 (Japan) high-resolution scanning electron microscope with an attachment for transmission microscopy.

The carbon composites were prepared for vacuum annealing using coal toluene (OAO Bagleikoks, Ukraine). The carbon mass (0,4 g) was mixed with 50 ml of toluene and filtered on a finely disperse biological filter and then dried in a drying oven at 60 °C. The amorphous carbon was removed by three-stage vacuum annealing at 220–870 °C in a laboratory vacuum furnace with a System VII-series graphite electrode from Contorr Vacuum Industries (USA). The temperature was 220 °C in the first stage, 550 °C in the second, and 870 °C in the third stage.

## Results and discussion

At the initial stage of the study, carbon modifications with amorphous structure were obtained from the plant material at the pyrolysis temperature of 950°C. The chemical composition of the amorphous carbon obtained by pyrolytic treatment of brown (rusty) sphagnum peat moss is given in the Table 1.

Table 1

The chemical composition of the amorphous carbon obtained by pyrolytic treatment of brown sphagnum peat moss

| | | Content*, wt. % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Spectrum, No | | O | C | W | Ni | Cu | Co | Fe | Ti |
| 1 | | 0,10 | 99,5 | 0,020 | 0,003 | 0,011 | 0,004 | 0,011 | 0,002 |
| 2 | | 0,12 | 99,3 | 0,010 | 0,001 | 0,015 | 0,005 | 0,015 | 0,005 |
| 3 | | 0,14 | 99,4 | 0,009 | 0,001 | 0,018 | 0,003 | 0,017 | 0,004 |

Note. *K, Na, Ca, Mg, Zn, Mn, Mo are also present in the analysis samples in traces.

In all cases, the morphology of the amorphous carbon is represented by the original structure typical for a specific type of plant material (Fig. 1).

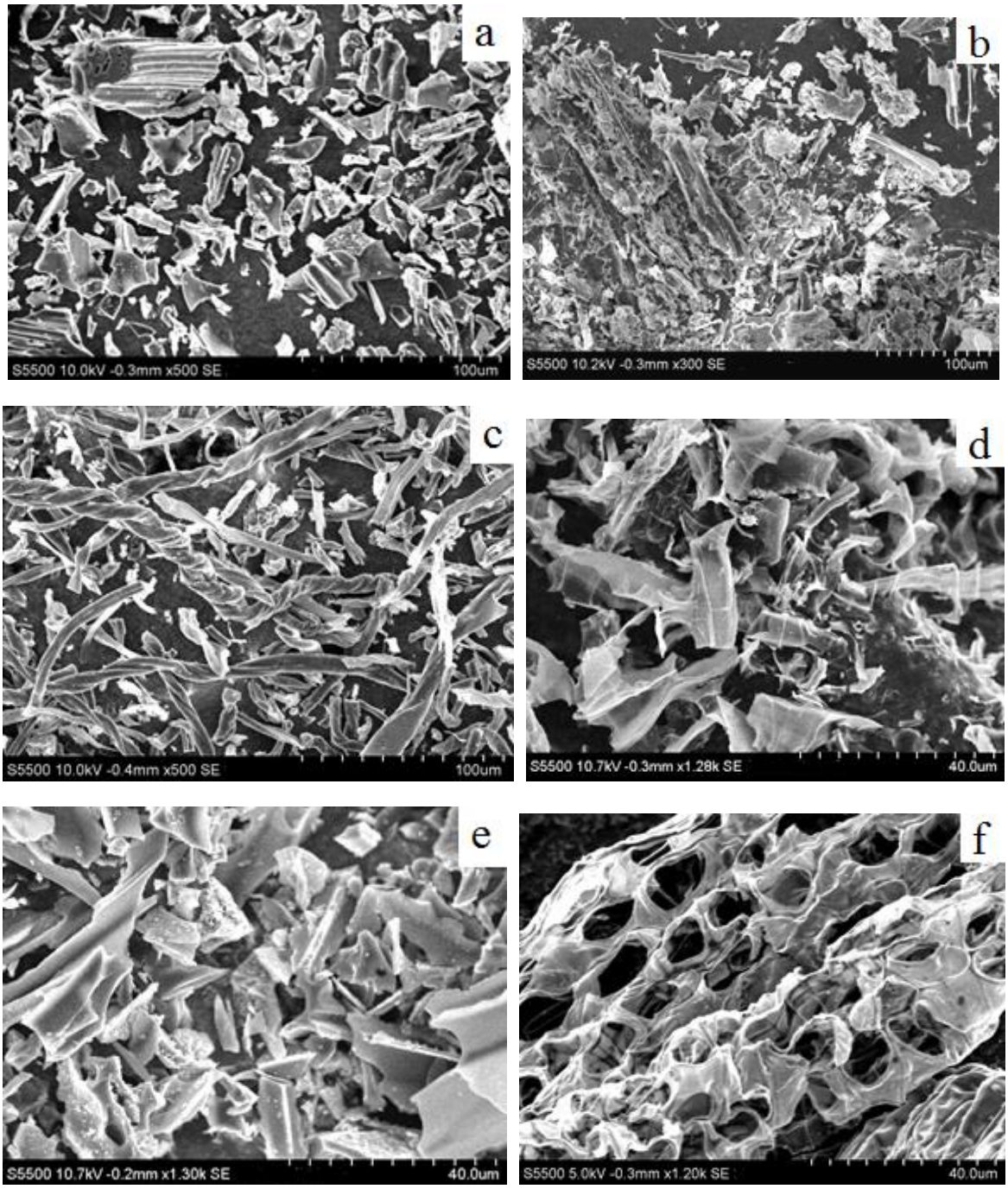


**Fig. 1. Structure (SEM) amorphous carbon after pyrolysis at 950 °C: a – spiny bamboo; b – corn; c – cotton; d – Magellan's peat moss; e – okra stalks; f – sphagnum brown.**

To ascertain the sequence of MCNT formation, the amorphous carbon was submitted to mechanical activation for 1 to 46 h. The change in the structure of the amorphous carbon in the course of its mechanical treatment in a vario-planetary mill is shown in Fig. 2.

As can be seen from Fig. 2, a, in the first 1–6 h, formation of MCNT is not discernible by electron microscopic methods (the amorphous carbon retains its lamellar form). After 8 h of treatment (see Fig. 2, b), begins the process of formation of a nanofiber structure, which is realized in the mass of the carbon particle (see Fig. 2, c), whereupon carbon nanotubes with diameters of 10–20 nm are formed.

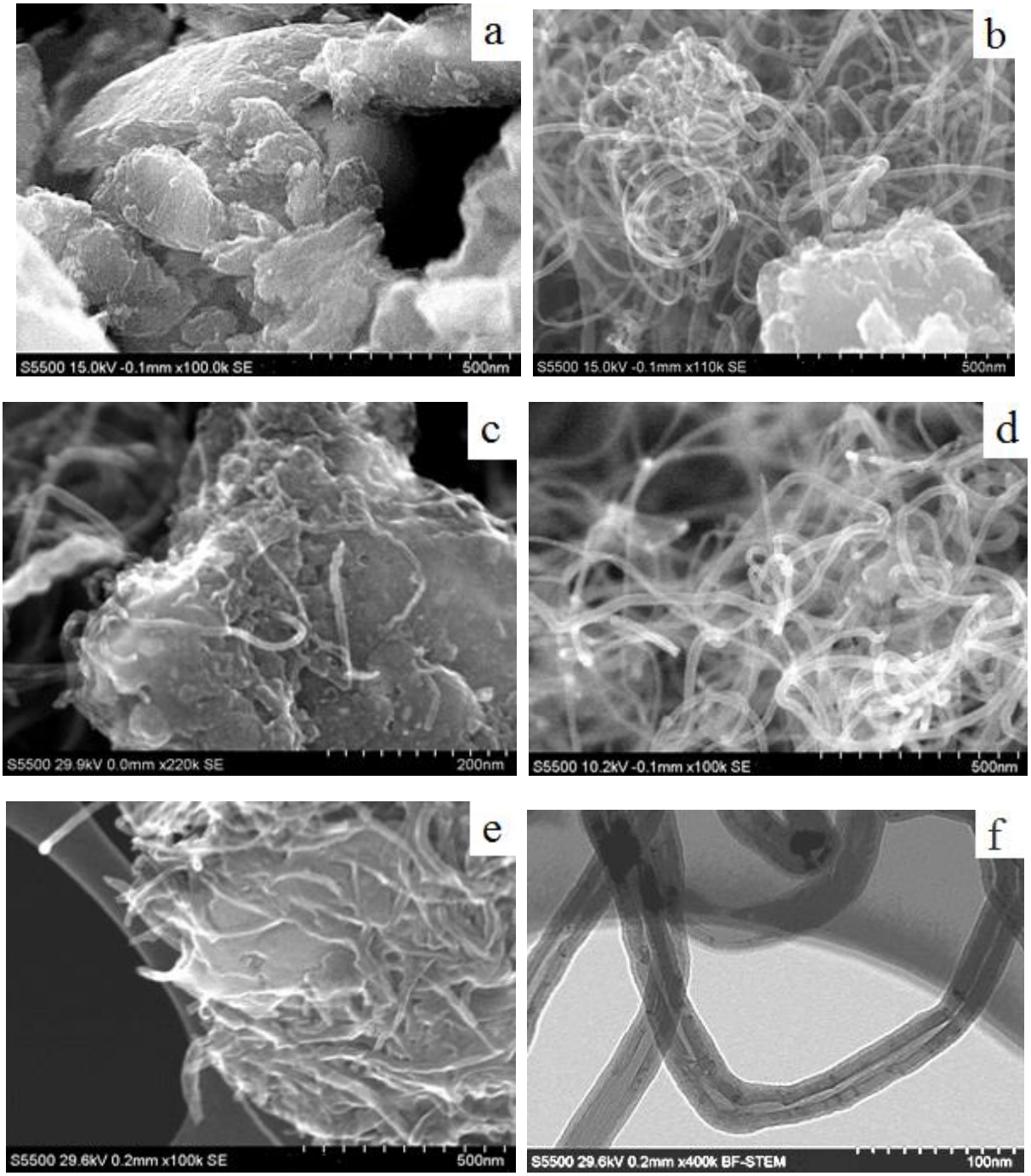


**Fig. 2. Change in structure of carbon from brown sphagnum peat moss (a–d and f) and corn (e) after mechanical activation for: a – 6 h; b, c – 8 h; d – 10 h; e – 16 h; f – 27 h; a, b, c, d – SEM image; f –TEM image.**

After 10 h of mechanical activation, the whole volume of the treated material consists of carbon nanotubes with diameters ranging from 10 to 70 nm (Fig. 2, d).

Note that some particles up to 3 μm in size survive up to 16 h of mechanical treatment (Fig. 2, e) when amorphous carbon is produced by pyrolysis of corn and Magellan's peat moss and up to 27 h when amorphous carbon from cotton plant, bamboo, and okra are used. Further extension of mechanical treatment time to 27 h leads only to increased defects in the carbon nanotubes with partial formation of "enclosed nanocones" and "bamboo" type of structures (Fig. 2, f). The MCNTs produced by mechanical activation of amorphous carbon have a fairly large specific surface area ($S_{sp}$= 400–510 $m^2/g$) and a low ash content (~ 1,5 wt. %).

It was shown earlier that the quantity of nanotubes formed upon mechanical activation of amorphous carbon depends linearly on the time of mechanical treatment (1–27 h) of carbon composite in a vario-planetary mill [6, 9]. To determine the nanotube content in the carbon composite, we carried out in this work three-stage vacuum annealing of the latter, which facilitates removal of amorphous carbon [8]. It is well known that carbon nanotubes retain thermal stability during high-temperature vacuum annealing up to 1900 °C and even above and that no change in morphology of the nanotubes occurs after thermovacuum treatment, which allows one to effectively purify CNTs and get a product with a purity of no less than 99,9 wt. % [2, 3].

As will be seen from Table 2, a substantial quantity of MCNT is formed in just 4 h of mechanical activation of the amorphous carbon, although electron microscopic methods do not show them up until 8 h of mechanical activation. The reason for this is MCNT formation inside the amorphous carbon particles. The yield of nanotubes reaches the maximum for all the studied amorphous carbon modifications when the duration of mechanical activation is 36 h.

Table 2

**Content of carbon nanotubes (wt. %) in carbon composite after vacuum annealing as a function of the mechanical-activation time**

| Initial plant matter | Mechanical-activation time, h | | | | | | |
|---|---|---|---|---|---|---|---|
| | 4 | 7 | 10 | 16 | 27 | 36 | 46 |
| Magellan's peat moss | 13,42 | 23,98 | 25,4 | 27,54 | 33,42 | 37,26 | 8,26 |
| Cotton | 4,14 | 8,45 | 21,84 | 24,25 | 26,55 | 28,72 | 7,12 |
| Okra stalks | 2,16 | 6,28 | 7,31 | 8,5 | 10,77 | 12,42 | 6,21 |

In this case, the MCNT content is found to be maximum (79,48 wt. %) after vacuum annealing of carbon composite obtained by mechanical activation of rusty (brown) sphagnum peat moss pyrolysis products (Fig. 3).

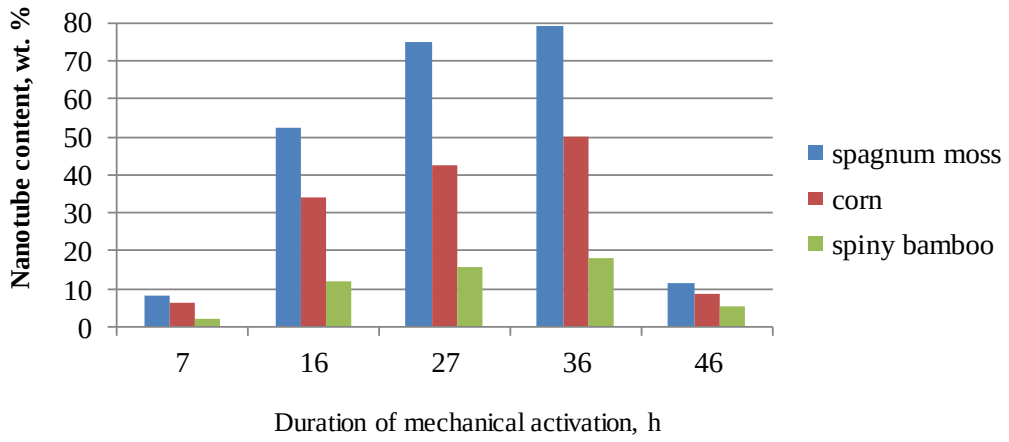


**Fig. 3. Nanotube content in carbon composite after vacuum annealing as a function of duration of mechanical activation of amorphous carbon.**

The results of scanning electron microscopic study of MCNTs formed upon 36- and 48-h of mechanical activation of the amorphous carbon produced from rusty (brown) sphagnum peat moss are shown in Fig. 4. In this case, the carbon composites were not submitted to vacuum annealing. As can be seen, the carbon nanotubes formed in 36 h of mechanical activation are segregated from each other, and formation of agglomerates and aggregates in the carbon material mass is not observed.

Extension of mechanical activation time to 46 h leads to formation of 20–100 nm tomentose aggregates (nanocomposites) consisting of carbon nanotubes and amorphous carbon. The aggregates are formed apparently due to electrostatic interaction of MCNTs. If this carbon nanocomposite is submitted

to vacuum annealing for removing amorphous carbon, the nanotube content in the annealing products decreases several folds (see Table 2, Fig. 3).

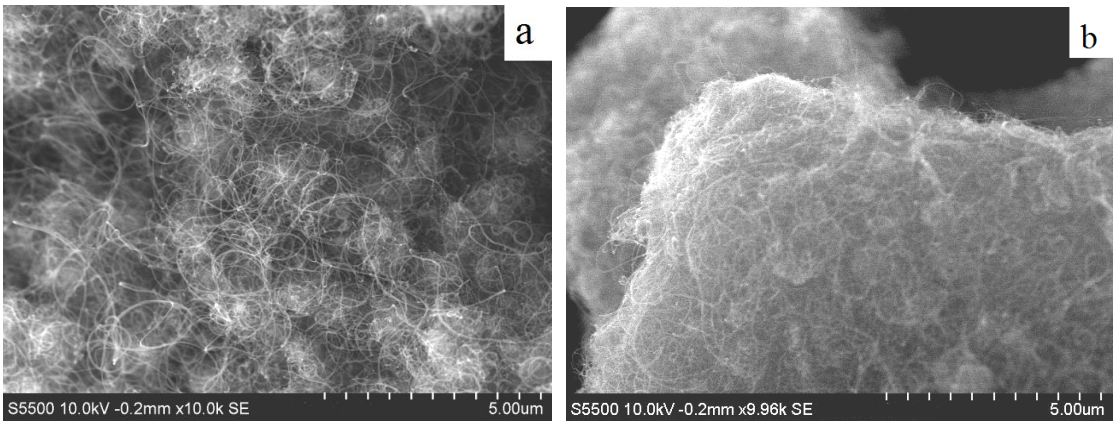


**Fig. 4. Structure (SEM) of carbon nanotubes obtained by mechanical activation for: a – 36 h; b – 46 h**

## Conclusions

Thus, the maximum carbon nanotube yield is observed after 36 h of mechanical activation of amorphous carbon obtained by pyrolysis of plant materials. Longer mechanical activation produces MCNT + amorphous carbon nanocomposite aggregates, which subsequently leads upon vacuum annealing to loss of thermal stability of the carbon nanotubes constituting the aggregate. This fact has to be taken into consideration while optimizing the technology of production and purification of carbon nanotubes formed from plant materials treatment products and while using MCNTs as modifiers of composites submitted to thermal action.

REFERENCES

1. Balasubramanian K., Burghard M. Biosensors based on carbon nanotubes. Analytical and Bioanalytical Chemistry. 2006(385);3:452-468.
2. Huang W., Wang Y. 99.9% purity multi-walled carbon nanotubes by vacuum high-temperature annealing, Carbon. 2003(13);41:2585-2590.
3. Lin C.-P., Lin J.-Z. Shu C.-M., Tseng J.-M. Multi-walled carbon nanotube thermal stability characteristics evaluation by DSC tests, Journal of Loss Prevention in the Process Industries. 2012(20);25:302-308.
4. Martinez-Hernandez A.L., Velasco-Santos C., Castano V.M. Carbon Nanotubes Composites: Processing, Grafting and Mechanical and Thermal Properties. Current Nanoscience. 2010(1);6:12-39.
5. Onishchenko D.V., Reva V.P. Creation of useful carbon materials from plants. Coke and Chemistry. 2012(5);55:192-196. DOI: 10.3103/S1068364X12050079
6. Onishchenko D.V., Reva V.P. High-energy treatment of sphagnum moss to produce carbon sorbents. Coke and Chemistry . 2012(10);55:396-398. DOI: 10.3103/S1068364X12100079
7. Onishchenko D.V., Reva V.P., Kuryavyi V.G. Hydrogen storage in multilayer carbon nanotubes. Coke and Chemistry. 2013(5):56:182-185. DOI: 10.3103/S1068364X13050049
8. Onishchenko D.V., Reva V.P., Kuryavyi V.G. Vacuum annealing of carbon nanotubes produced from amorphous carbon. Coke and Chemistry. 2012(12); 55:467-469. DOI: 10.3103/S1068364X12120034
9. Onishchenko D.V., Reva V.P., Voronov B.A. Adsorption activity of carbon nanotubes formed from brown sphagnum moss in mechanical activation, Journal of Analytical Chemistry. 2014(5);69:403-407. DOI: 10.1134/S1061934814050074
10. Popov V.N. Carbon nanotubes: Properties and application. Materials Science and Engineering R: Reports. 2004(3);43:61-102.
11. Terrones M. Science and Technology of the Twenty-First Century: Synthesis, Properties, and Applications of Carbon Nanotubes. Annual Review of Materials Research. 2003;33:419-501.
12. Zhang Y., Bai Y., Yan B. Functionalized carbon nanotubes for potential medicinal applications. Drug Discovery Today. 2010(11-12);15:428-435.

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# Продукты пиролиза растительного сырья как ресурс для формирования углеродных нанотрубок

**Аннотация:** Представлен анализ влияния продолжительности механической активации аморфного углерода (1–46 ч) на морфологию формируемых многослойных углеродных нанотрубок. Показано, что длительное механическое активирование углеродного композита в варио-планетарной мельнице способствует образованию агрегатов, что приводит к потере термостабильности сформированных углеродных нанотрубок при последующим проведении вакуумного отжига.
*Ключевые слова:* пиролиз, аморфный углерод, механоактивация, многослойные углеродные нанотрубки, композит.

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